Synthesis and Characterization of ZIF 67 CTAB-Assisted for Supercapacitor Electrode Active Material

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Abstract. This study investigates the influence of adding hexadecyltrimethylammonium bromide (CTAB) on the morphology and electrochemical performance of ZIF-67. The addition of CTAB results in smaller ZIF crystal sizes, which enhances the diffusion capability of electrolyte ions. ZIF-67 synthesized with and without the addition of CTAB was characterized using X-ray diffraction and scanning electron microscopy to confirm the material's crystallinity and morphological structure. Electrochemical performance was tested through cyclic voltammetry to determine the redox peak current and galvanostatic charge-discharge to calculate the specific capacitance based on the discharge time. The findings revealed that CTAB enhances crystallinity, as observed in XRD analysis, and reduces particle size from an average of 1692 nm to 1057 nm, as measured by SEM. Electrochemical testing further demonstrated that the addition of CTAB during ZIF-67 synthesis increased the specific capacitance of active material from 98 Fg^{-1} to 105 Fg^{-1} at a current density of 1 $Ag^{-}1$ in a 3M KOH. Based on these results, CTAB-assisted ZIF-67 shows promising potential for further development as an active electrode material, which could lead to new derivative materials as candidates for supercapacitor electrodes.

Keywords: *CTAB, Supercapacitor, Zif-67, Energy storage*

1 Introduction

The energy crisis, rising air pollution, and global warming resulting from the use of fossil and coal-based energy have accelerated the advancement of sustainable and eco-friendly energy sources. This approach aims to reduce negative environmental impacts and ensure sustainable energy availability for future generations Holechek *et al.* [1]. Supercapacitors are a relatively an innovative

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type of energy storage devices that perform between rechargeable battery and conventional capacitor, offering faster charge and discharge capabilities. Supercapacitors offer several advantages, including the ability to provide high power and energy, a long cycle life, the capacity to operate over a wide temperature range, and environmental friendliness Wei *et al.* [2]. These benefits make supercapacitors an appealing choice for various sustainable energy applications and modern electronic devices.

Metal Organic Frameworks (MOF) are materials formed from bonds between organic and inorganic materials, composed of metal ions cluster and organic ligands. MOF are characterized by their porous nature, large surface area, and ease of synthesis, making them promising candidates for energy storage technology development Shi *et al.* [3]. Zeolitic Imidazolate Framework-67 is a type of MOF that contains cobalt as the central atom and 2-methylimidazole as the ligand. This material stands out due to its abundant porosity and high surface area, as well as its good stability and simple synthesis process. However, ZIF-67 has limitations in terms of conductivity. To address these shortcomings, ongoing research aims to improve its electrochemical performance, either by incorporating additional metal materials, producing derivative materials such as metal oxides, nanoporous carbon, sulfides, or phosphates, or by physically modifying the material itself.

Studies on the effect of ZIF-67 morphology for supercapacitor applications remain limited. Akram Hosseinian *et al.* reported in [4] that the performance of the synthesized dodecahedral-shaped bare ZIF-67 achieved a specific capacitance of 103.9 Fg^{-1} at 1 Ag^{-1} and through long-cycle testing, it achieved a capacitance retention of 59% after 1000 cycles at 10 Ag^{-1}. Daojun Zhang et al. in [5] employed a synthesis strategy to produce ZIF-67 with a microflower structure, based on GCD electrochemical testing, it has a specific capacitance of 188.7 Fg^{-1} at a current density 1 Ag^{-1}. Wenjie Cao in [6] reported the successful synthesis of ZIF-67 with nanocube morphology, which showed a specific capacitance of 28.76 Fg^{-1} at a current density of 1 Ag^{-1} and exhibited high stability after 1000 cycles during performance testing.

This study compares the crystal morphology and electrochemical properties of ZIF-67 synthesized with and without the addition of CTAB, aiming to modify its morphology and particle size. This adds a new perspective for further research development in the field of electrochemical supercapacitor applications.

2 Methodology

2.1 Synthesis Material

ZIF-67 was synthesized using co-precipitation method by dissolving 0.58 gr cobalt nitrate hexahydrate as the metal ion source (Sigma Aldrich) in 20 mL of water, designated as Solution A. Separately, 9.08 gr of 2-methylimidazole (Sigma Aldrich) was dissolved in 140 mL of water, designated as Solution B. Both solutions were stirred individually using a magnetic stirrer for 30 minutes. Solution A was then added to Solution B, with stirring continued for an additional 30 minutes. The resulting mixture formed a purple solution, which was left to precipitate at room condition for 24 hours. The precipitate was then washed several times using a centrifuge to ensure the purity of the material.

The synthesis process of CTAB-Assisted ZIF-67 followed the same procedure. However, 0.005 gr of CTAB was added to Solution A, and the process was continued as previously described until the washing step. The final product was then dried in a vacuum oven at 60°C for 48 hours to ensure complete removal of any residual, resulting in a stable, dry material ready for further analysis.

2.2 Electrode Preparation

The synthesized ZIF-67 active material was utilized in the preparation of the working electrode (WE). Working electrode was made by mixing 4 mg of ZIF-67 active material, 150 µL of 2-propanol, 800 µL of aqueous solution and 50 µL of Nafion™ perfluorinated resin solution, then dispersed using an ultrasonic instrument for 30 minutes until a homogeneous solution was obtained. A volume of 250 µL of the active material solution was then deposited onto carbon paper (1 cm x 1 cm), followed by drying for 6 hours at 60°C. All electrochemical experiments were performed using a conventional three electrode configuration, with a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference.

2.3 Characterization and Electrochemical Performance

The morphology of the synthesized ZIF-67 and CTAB-assisted ZIF-67 materials was analyzed using Scanning Electron Microscope (SEM) a Quanta 650 by Thermo Fisher Scientific. The structural characteristics of the synthesized

materials were examined using a Bruker D8 Advanced X-ray Diffractometer for X-ray diffraction (XRD) analysis with Cu Kα radiation (λ=1.54 Å). Electrochemical measurements in a three-electrode configuration were carried out using the CH Instrument 660E electrochemical workstation, a specialized electrochemical analyser. The electrochemical performance of the materials was thoroughly investigated through a series of cyclic voltammetry and Galvanostatic charge-discharge. These tests were conducted in a 3 M KOH, with potential window set between 0.00 - 0.5 V for CV measurements and between 0.00 - 0.45 V for GCD, to analyse the electrode's behaviour under these specific conditions.

3 Results and Discussion

3.1 XRD and SEM Characterization.

The crystal structures of the synthesized ZIF-67 and CTAB-assisted ZIF-67 were measured using X-ray diffraction (XRD) with a 2θ range from 5 to 40°, as shown in Figure 1. The diffraction peaks of the material around 2θ = 7°, 10°, 12°, 14°, 16°, 17°, 22°, 24°, 25°, 26°, 29°, 30°, 31°, 32°, 34°, 36°, 37°, and 38° correspond to the crystallographic planes (011), (002), (112), (022), (013), (222), (114), (233), (224), (134), (044), (334), (244), (116), (226), (444), (345), and (127), according to COD reference number 7222297 by J. Narimbi *et al*. in [7]. This indicates that the synthesis of ZIF-67 was successfully achieved both with and without the use of CTAB. The distinct and sharp peaks suggest that the samples possess a high level of crystallinity. Moreover, the addition of CTAB did not result in any new diffraction peaks, suggesting that the formed ZIF-67 material maintains identical bonding structures.

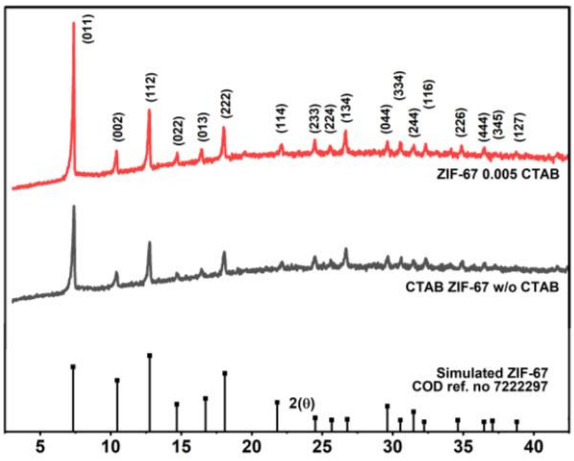

Figure 1. XRD Pattern of ZIF-67 and ZIF-67 CTAB-Assisted

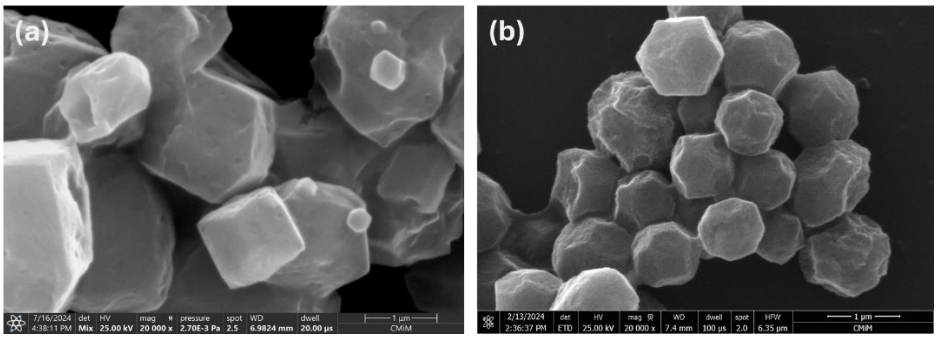

Figure 2 ZIF-67 without CTAB (a), ZIF-67 CTAB-Assisted (b)

The morphology of the synthesized ZIF-67 material was analyzed through scanning electron microscopy (SEM), and the observed structural details are presented in Figure 2. It can be observed that ZIF-67 synthesized with the addition of the surfactant CTAB exhibits smaller and more uniform rhombic dodecahedral-shaped particles compared to ZIF-67 synthesized without CTAB. This is due to the surfactant properties of CTAB, which limit crystal growth in specific directions and accelerate the reaction process as reported by Y. Chen *et al.* in [8]. The synthesis process using CTAB led to a decrease in the average particle size from 1692.9 nm to 1057.08 nm. This finding aligns with previous research by Y. Pan *et al.* in [9] which reported that the use of CTAB leads to smaller particle sizes in the formation of ZIF-67.

3.2 Electrochemical Performance

The electrochemical performance of the material was assessed using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests conducted in a 3M KOH. The cyclic voltammetry tests were conducted over a potential range of 0.0 V - 0.5 V, with different scan rates from 5 to 100 mV/s. A comparison of the CV curves at different scan rate is presented in Figure 3a and 3c, where distinct peaks can be observed, indicating the occurrence of oxidation and reduction processes. This behaviour is likely due to the uniform crystal formation and the effect of CTAB, which reduces particle size, allowing for faster ion transport. As the scan rate increases, the anodic peak shifts to a higher positive potential, while the cathodic peak moves to a more negative potential, indicating

oxidation and reduction events typical of faradaic pseudo capacitor behaviour Aoki, *et al.* [10], and Septiani *et al.* [11].

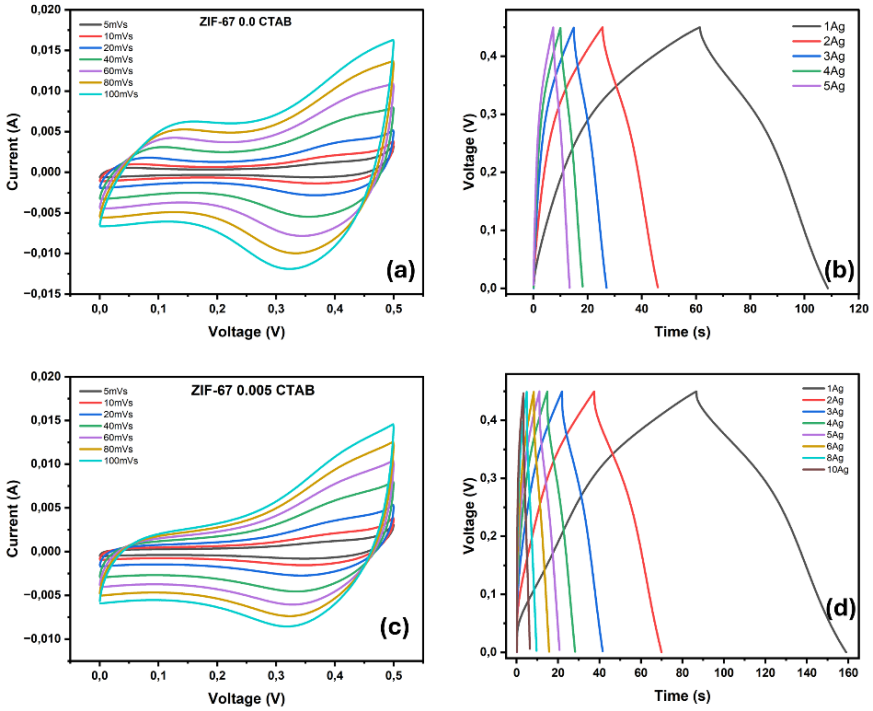

Figure 3 (a) CV Curve of ZIF-67 w/o CTAB, (b) GCD of ZIF-67 w/o CTAB, (c) CV Curve of ZIF-67 CTAB-Assisted, (d) GCD of ZIF-67 CTAB-Assisted

The galvanostatic charge-discharge (GCD) analysis for the ZIF-67 electrode material was conducted at a potential range of 0 – 0.45 V and a current density of 1–5 Ag^{-1}. The charge-discharge curves, as shown in Figures 3b and 3d, reflect the redox reactions occurring on the surface of the ZIF-67 material. The specific capacitance was determined from the GCD curves using the discharge time as a basis for calculation. The ZIF-67 material without the CTAB surfactant achieved a specific capacitance of 98 Fg^{-1} at a current density of 1 Ag^{-1}, while the ZIF-67 material with the addition of CTAB increased to 105 Fg^{-1} under the same current density, This is likely due to morphological structural changes that allow ions to more easily reach active sites, thereby contributing to an increase in active sites. It is evident that specific capacitance decreases as the current density increases. This occurs because, at lower current densities, a greater number of OH^- ions can access the electrode's active sites through the diffusion process. Kaushik *et al.* [12].

4 Conclusion

The ZIF-67 material was successfully synthesized using the coprecipitation method, both with and without the addition of the CTAB surfactant. The ZIF-67 synthesized with CTAB displayed a more uniform rhombic dodecahedral morphology with a consistent particle size of 1057.06 nm. The electrochemical performance of ZIF-67 synthesized with 0.005 gr CTAB showed an improved specific capacitance of 105 Fg^{-1} at a current density of 1 Ag^{-1} in a 3M KOH electrolyte. These results suggest that ZIF-67, with the addition of CTAB, holds promise as an active material for supercapacitors electrode or as a precursor for the development of derivative materials. Further exploration of its potential in various energy storage applications could be a valuable direction for future research.

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